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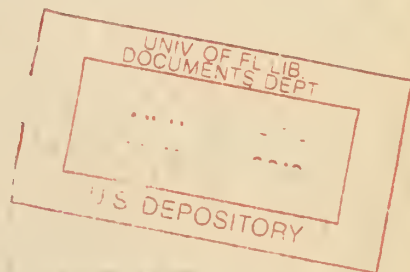
**(Part A - Additional tests on Anodized Aluminum and on
Zinc-Chromate-Primed Magnesium)**

February 1955



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AIR FORCE-NAVY-CIVIL SUBCOMMITTEE
on
AIRCRAFT DESIGN CRITERIA
Under the Supervision of the
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MUNITIONS BOARD**

No. 1842-A



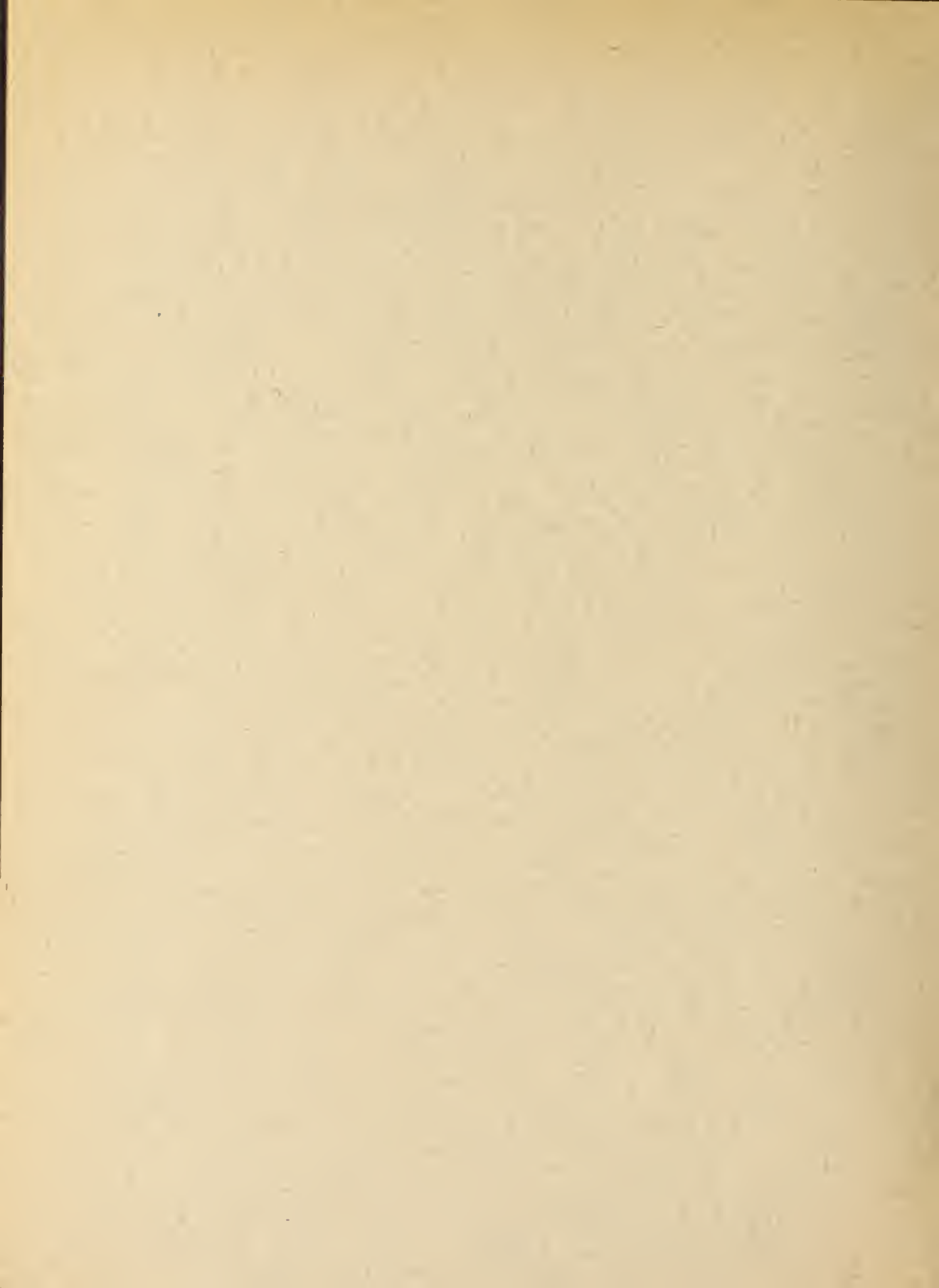
**UNITED STATES DEPARTMENT OF AGRICULTURE
FOREST SERVICE
FOREST PRODUCTS LABORATORY**

Madison 5, Wisconsin

In Cooperation with the University of Wisconsin

MAR 16 1955

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ADHESIVE BONDING PROPERTIES OF VARIOUS METALS AS AFFECTED BY
CHEMICAL AND ANODIZING TREATMENTS OF THE SURFACES¹

(Part A--Additional tests on Anodized Aluminum and on
Zinc-Chromate-Primed Magnesium)

By

H. W. EICKNER, Chemical Engineer

Forest Products Laboratory,² Forest Service
U. S. Department of Agriculture

Summary

The concentration of chromic acid (5 or 10 percent) and the length of the anodizing period (20 or 40 minutes) were not found to influence the adhesive bonding properties of the chromic-acid-anodized, bare 75S-T6 aluminum alloy. However, seal treatment of the anodized surface by heating in water greatly interfered with bonding except for one type of adhesive (high-temperature formulation of neoprene, nylon, and phenol resins on fabric carrier). This same adhesive also gave unusually good bonding to zinc-chromate-primed magnesium surfaces with bond strengths averaging as high as 2,770 pounds per square inch on the standard 1/2-inch overlap specimens of 0.064-inch-thick FSl-H magnesium.

Introduction

The following tests were made to supplement the previous work on adhesive bonding of various metal surfaces reported in Forest Products Laboratory

¹-This progress report is one of a series prepared and distributed by the Forest Products Laboratory under U. S. Navy Bureau of Aeronautics Order No. NAer 01628 and U. S. Air Force Order No. AF 18(600)-102, Amendt. No. A6(55-286). Results here reported are preliminary and may be revised as additional data become available.

²-Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

Report No. 1842.³ These new tests include work to determine the effect of chromic acid concentration (5 or 10 percent by weight), length of treatments (20 or 40 minutes), and hot-water sealing in anodizing bare 75S-T6 aluminum, on the initial bond strength of joints to this metal. Adhesive bonding tests were also made on magnesium surfaces that had been treated and zinc-chromate-primed by two aircraft fabricators using their standard surface treatments. The zinc-chromate-prime coatings used with these treatments were thinner than those used on magnesium surfaces in the previous work in Report No. 1842, and were reported to improve bonding to this metal.

Procedure

Type and Number of Specimens

Small 4- by 5-1/2-inch test panels were prepared by overlapping two 3- by 4-inch metal sheets, 0.064-inch in thickness, for 1/2 inch. Metal sheets of 2 types, bare 75S-T6 aluminum alloy and FSl-H24 magnesium alloy, were included in these tests. Three test panels were bonded for each of the variables studied with three 1-inch-wide test specimens cut from each of the panels.

Preparation of Metal Surfaces

Aluminum.--The bare 75S-T6 aluminum surfaces were prepared for bonding by first wiping with a cloth saturated with acetone, and then immersing for 5 minutes at 170° to 190° F. in an alkaline solution (pH approximately 12.0) of the composition:

5.0 ounces sodium metasilicate
0.5 ounce Nacconal NR
1.0 gallon water

The alkaline solution was rinsed from the surfaces in hot water and then cold water. The sheets were then anodized in a chromic acid solution (5 or 10 percent by weight) at 90° to 100° F. by first applying a small direct current potential (3 to 5 volts) between the aluminum pieces suspended as anodes and the cathode, which was the lead container for the solution. This voltage was gradually increased (within 5 minutes) to 40 volts. The higher voltage was applied at a current density of 2.5 to 3.0 amperes per square foot of anode surface for periods of 20 or 40 minutes.

³Eickner, H. W. Adhesive Bonding Properties of Various Metals as Affected by Chemical and Anodizing Treatments of the Surfaces. Forest Products Laboratory Report No. 1842.

After removal from the anodizing treatment, the surfaces were either rinsed in warm water and force dried in front of a circulating fan (unsealed), or sealed by heating the metal sheets in distilled water for 1 hour at 180° F. before drying.

With the use of 2 concentrations of anodize solution, at 2 anodizing periods for both sealed and unsealed surfaces, 8 types of anodized aluminum surfaces were therefore prepared for investigation in this study.

Magnesium.--The surfaces of the magnesium sheets were prepared for bonding by two aircraft fabricators by using their established procedures.

A. One method, involving electrolytic treatments, was reported to consist essentially of the following steps:

- (1) Vapor degreasing surfaces in stabilized trichloroethylene to remove oils and contaminants
- (2) Cathodic cleaning (4.0 to 6.0 volts direct current at 5 to 25 amperes per square foot of cathode surface) for 3 to 10 minutes at 180° to 200° F. in a solution of the composition:

10.0 ounces sodium hydroxide
1.0 gallon water
- (3) Rinse in cold water
- (4) Pickling for 3 to 5 seconds at room temperature in a solution of the composition:

4.3 ounces concentrated sulfuric acid (sp. gr.-1.84)
2.8 ounces concentrated nitric acid (sp. gr.-1.42)
1.0 gallon water
- (5) Rinse in cold water
- (6) Electrolytic treatment for approximately 15 minutes with a 4.0- to 8.0-volt, 60-cycle alternating current at a current density of 20 to 30 amperes per square foot of magnesium surface in a solution of the composition:

40.0 ounces sodium hydroxide
0.5 ounce phenol
5.2 ounces sodium silicate (41° Be.)
Water to make 1 gallon
Operating temperature of the solution was 180° to 200° F.
- (7) Rinse in hot water

- (8) Neutralizing for 1 to 5 minutes at 135° to 145° F. in solution (pH-2.4) of the composition:

0.07 ounce chromic acid
1.0 gallon water
- (9) Force drying in hot air
- (10) Priming by dipping in a zinc chromate primer (MIL-P-6889A, Type I) thinned to result in a dry film thickness of 0.00020 to 0.00035 inch
- (11) Air drying prime coat for at least 24 hours prior to bonding.

B. The other method, involving only chemical treatments, was reported to consist essentially of the following steps: (Metal pieces with this method were slightly larger, 5- by 6-inches, than the standard size.)

- (1) Vapor degreasing surfaces in stabilized trichloroethylene to remove oils and contaminants
- (2) Cleaning surfaces by immersion for 10 minutes at 170° to 190° F. in a commercial phosphoric-silicate cleaner for magnesium (5 ounces per gallon)
- (3) Rinse in cold water
- (4) Removing scale by immersion for 1 to 10 minutes at room temperatures in a solution of the composition:

24.0 ounces chromic acid
4.0 ounces sodium nitrate
1.0 gallon water
- (5) Rinse in hot water
- (6) Pickling for 5 minutes at room temperature in a solution of the composition:

1 part by volume hydrofluoric acid (50 percent)
2 parts by volume water
- (7) Rinse in cold water
- (8) Sealing by boiling for 30 minutes in a solution of the composition:

16.0 ounces sodium dichromate
0.2 ounce calcium fluoride
1.0 gallon water

- (9) Rinse in cold water
- (10) Forced drying in hot air
- (11) Priming by dipping in zinc chromate primer, thinned with toluene (1 part primer to 3 parts thinner) to a consistency to result in a dry film thickness of 0.00015 to 0.00025 inch
- (12) Air drying prime coat 24 hours, and then curing for 30 minutes at 180° to 200° F.

These two methods were essentially the same as methods M-5 and M-3, respectively, in the original work of Report No. 1842, except that the prime coat in the earlier work was much thicker, and different proprietary primers were used.

Adhesive Bonding Processes

The following 4 adhesive bonding processes were used in bonding the lap-joint panels prepared with the 2 metals having several surface conditions.

Bloomingtondale FM-47.--A high-temperature-setting formulation of the vinyl-phenolic type supplied by Bloomingtondale Rubber Company, Delaware and Flower St., Chester, Pa.

Redux E, Type R.--A high-temperature-setting, two-component formulation of a phenol-resin solution and vinyl-polymer powder supplied by Ciba Company, 627 Greenwich St., New York 14, N. Y.

Metlbond MN3C Nylon Tape.--A high-temperature-setting adhesive formulation of neoprene, nylon, and phenol resins, supported as a film on nylon-fabric tape, supplied by NARMCO Resins and Coatings Company, 600 Victoria St., Costa Mesa, Calif.

Scotchweld Bonding Film AF-6.--A high-temperature-setting formulation of acrylonitrile-butadiene rubber and phenol resin in the form of an unsupported tape supplied by Minnesota Mining and Manufacturing Company, 411 Piquette Ave., Detroit, Mich.

These adhesives are of the same general types as used in the original studies of Report 1842 and addendum, but the adhesive products included are identical in only 1 of the 4 processes.

The conditions of bonding with each of the adhesives were as follows:

Bloomingtondale FM-47.--Three spray coats of the adhesive, thinned with 1-1/2 parts by volume of adhesive solvent to 1 part of adhesive, were

applied to the metal with 1-hour air drying between coats, and overnight air drying after the final coat. The adhesive film was then precured for 1 hour at 150° F. in an oven. Following the precure, the joint was assembled and placed in a hot press, where it was preheated without pressure for 5 to 9 minutes at 300° F. before it was given the final cure for 15 to 25 minutes at 300° F. and 200 pounds of pressure per square inch.

Redux E, Type R.--One medium coat of the liquid component was brushed on the metal, and the powdered component was sprinkled immediately into the wet spread of adhesive. Any excess powder was brushed from the surface. The adhesive film was air dried overnight, and the joint was assembled and pressed at 200 pounds per square inch of pressure for 25 minutes in a hot press at a temperature of 300° F. Approximately 10 minutes of the pressing period were required to bring the temperature of the glue line to that of the press platen.

Metlbond MN3C Nylon Tape.--Four spray coats of the priming component (M3C) were applied to the metal pieces to result in a 0.001- to 0.002-inch film of adhesive. The adhesive film was dried for 30 minutes between coats and 2-1/2 to 4 hours after the final coat. The joint was assembled with a single layer of tape adhesive and pressed at 50 pounds per square inch pressure for 42 minutes in a hot press at a temperature of 335° F. Approximately 12 minutes of the pressing period were required to bring the temperature of the glue line to that of the press platen.

Scotchweld Bonding Film AF-6.--The single film of adhesive was assembled in the joint. The assembly was pressed for 45 minutes at 150 pounds per square inch of pressure in a hot press at a temperature of 325° F. Approximately 10 minutes of the pressing period were required to bring the temperature of the glue line to that of the press platen.

To insure uniform pressure distribution, all joints were pressed by using cauls of 0.027-inch-thick chipboard between the press platen and the metal pieces.

Testing

The 3 lap-joint panels prepared with each metal, surface treatment, and bonding process were sawn into individual 1-inch-wide specimens. Cutting was done with a metal-cutting bandsaw using a slow rate of feed and a holding jig to minimize any mechanical damage or overheating of the joint. The lap-joint specimens were tested to failure by loading them in tension at a rate of 300 pounds per minute. The ends of the specimens were held in 1-inch-wide Templin-type grips that extended down from the ends of the specimens to within 1-inch of the edge of the overlap. Testing was done at a temperature of 72° to 76° F. The failing load (calculated as unit stress on the measured test area)

and estimated areas (expressed as percentage of the total area) of adhesion, cohesion, and primer and coating failures were recorded.

Test Results

The results of the bonding tests made to the chromic-acid-anodized aluminum, unsealed and sealed, are given in table 1, and to the zinc-chromate-primed magnesium in table 2.

The results in table 1 definitely show that the hot-water sealing of the aluminum oxide film formed during chromic-acid anodizing interferes with bonding. This interference is much greater for types of adhesives represented by Bloomingdale FM-47, Redux E, and Scotchweld Bonding Film AF-6 than it is for the type of adhesive represented by Metlbond MN3C Tape. The concentration of the chromic-acid anodizing solution (5 or 10 percent) and the length of the anodizing period (20 or 40 minutes) were not found to influence the bonding properties of the anodized surfaces significantly.

The results in table 2 again confirm the results indicated in the original work and given in Forest Products Laboratory Report No. 1842; namely, that adhesives of the type of Metlbond MN3C Tape produce bonds to zinc-chromate-primed magnesium sheets that usually have higher bond strengths than those obtained with the Redux E and Bloomingdale FM-47-type adhesives. The latter two types are normally judged by lap-joint tests with clad aluminum to have higher bond strengths than the first type. The type of solvent in an adhesive, and its reaction with the primer, might be expected to influence the bond strengths to the zinc-chromate-primed magnesium but this possible effect was not investigated. The average shear strength of 2,770 pounds per square inch for the bonds made with Metlbond Tape to the zinc-chromate-primed magnesium, treated by method B, is considered by present standards to be unusually good bonding to magnesium. The Metlbond Tape adhesive, and also Scotchweld AF-6 film, gave bond strengths of about 1,950 pounds per square inch to the magnesium treated by method A.

Table 1.--Results¹ obtained in adhesive bonding of sealed and unsealed chromic-acid anodized surfaces of bare 75S-T6 aluminum alloy

Anodize treatment		Test results ¹ for --									
		Bloomingtondale		Metlbond MN3C		Redux E,		Scotchweld film			
Concentra-:Anodize: Seal		FM-47		nylon tape		type R ²					
tion of :period :treatment:											
chromic											
acid											
		Average :Adhesion:		Average :Adhesion:		Average :Adhesion:		Average :Adhesion:			
		joint :failure ³ :		joint :failure ³ :		joint :failure ³ :		joint :failure ³ :			
		strength:		strength:		strength:		strength:			
Percent		P.s.i.		Percent		P.s.i.		Percent		P.s.i.	
		Min.									
5	:	20	:	:	:	:	:	:	:	:	:
	:	Boiling	:	:	:	:	:	:	:	:	:
	:	water ⁴	:	783	:	2,611	:	64	:	1,013	:
	:	None	:	4,406	:	3,474	:	18	:	4,326	:
	:	40	:	:	:	:	:	:	:	:	:
	:	Boiling	:	:	:	:	:	:	:	:	:
	:	water ⁴	:	869	:	2,799	:	71	:	776	:
	:	None	:	4,443	:	3,213	:	26	:	4,319	:
	:		:		:		:		:		:
	:		:		:		:		:		:
10	:	20	:	:	:	:	:	:	:	:	:
	:	Boiling	:	:	:	:	:	:	:	:	:
	:	water ⁴	:	655	:	2,641	:	77	:	1,246	:
	:	None	:	4,182	:	2,996	:	28	:	4,216	:
	:	40	:	:	:	:	:	:	:	:	:
	:	Boiling	:	:	:	:	:	:	:	:	:
	:	water ⁴	:	554	:	2,542	:	86	:	788	:
	:	None	:	4,483	:	3,251	:	22	:	4,171	:
	:		:		:		:		:		:
	:		:		:		:		:		:

¹Each value given is the average result for a total of 9 test specimens, 3 cut from each of 3 bonded panels, 4 inches wide, with 1/2-inch overlap of 0.064-inch-thick bare 75S-T6 aluminum alloy sheet.

²Redux E, type R, used in this part of the study was used with coarse-mesh powder supplied with the adhesive.

³Average estimate of the amount of bonded area in which failure was in adhesion between the adhesive and anodized metal.

⁴Seal treatment consisting of heating the anodized aluminum panels for 1 hour at 190° F. in distilled water. The Reynolds Metals Co. states on page 48 of its handbook, "Finishes for Aluminum," copyrighted 1949, that immersion in hot water of the porous oxide film produced in anodizing converts the oxide to the monohydrate that seals the pores of the film.

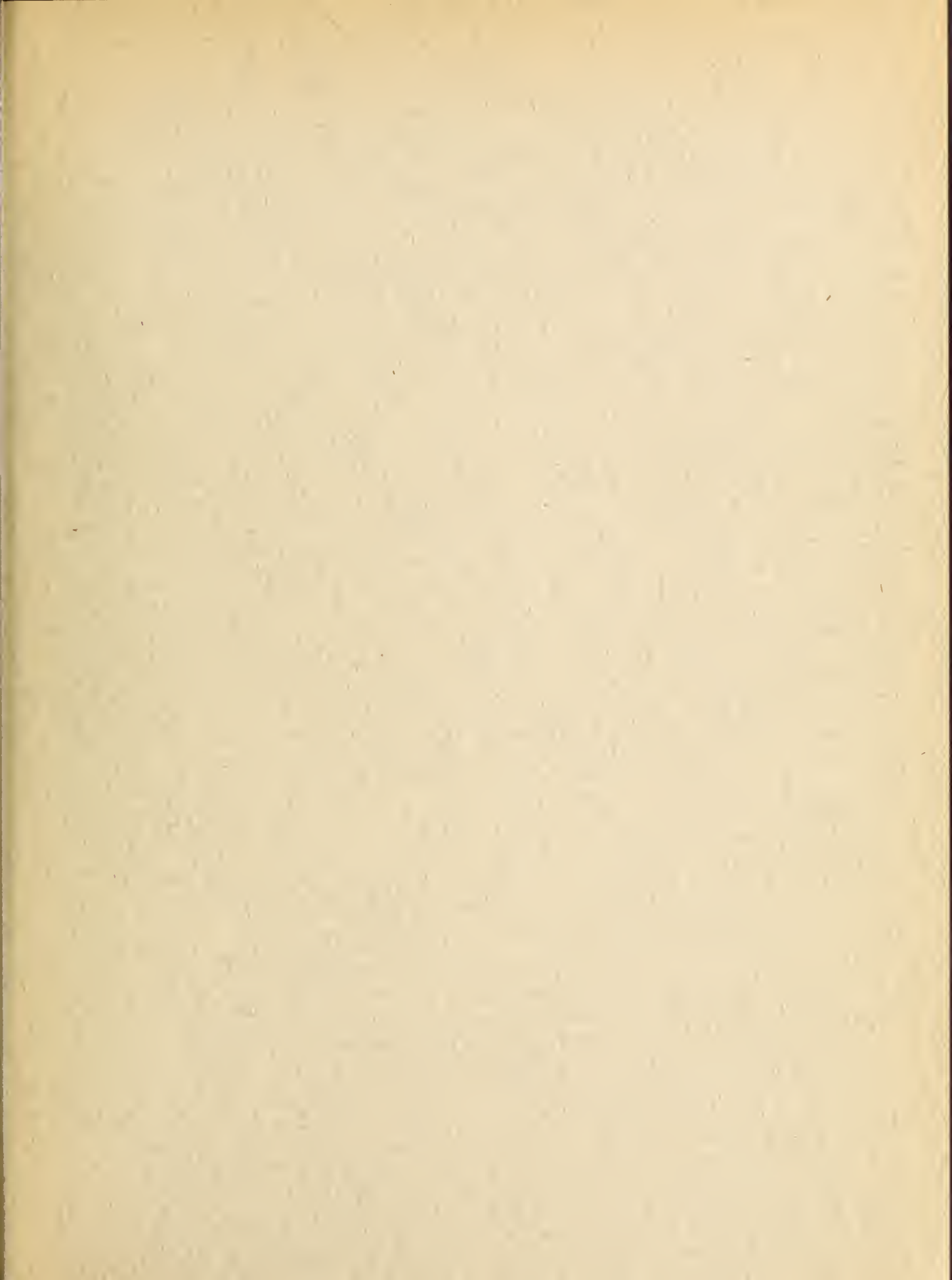
Table 2.--Results obtained in adhesive bonding of zinc-chromate-primed magnesium sheets

Adhesive	Method A - Electrolytic treatment ¹			Method B - Chemical treatment and seal ²		
	Average	Type of failure ³	Joint	Average	Type of failure ³	Joint
	strength	Cohesion	Adhesion	Primer	Cohesion	Adhesion
	:	:	to	:	:	to
	:	:	primer	:	:	primer
	:	:	coating	:	:	coating
	P.s.i.	Percent	Percent	P.s.i.	Percent	Percent
Bloomingdale FM-47	769	0	100	0	1,070	0
Metlbond MN3C:						
Nylon tape	1,934	15	85	0	2,770	15
Redux E, type R	167	0	100	0	835	44
Scotchweld AF-6 film	1,948	3	97	0	633	0

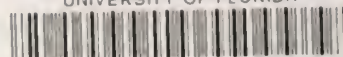
¹Test values given are the average for a total of 9 test specimens, 3 cut from each of 3 bonded panels, 4 inches wide, with a 1/2-inch overlap of 0.064-inch-thick magnesium sheet.

²Test values given are the average for a total of 12 to 15 test specimens, 4 or 5 cut from each of 3 bonded panels, 6 inches wide, with a 1/2-inch overlap of 0.064-inch-thick magnesium sheet.

³Average estimates of the type of failure in the areas of the bonded joint. The first two columns are for cohesion and adhesion failures of the adhesives, with the third column indicating failures of the primer or coating of the metal.



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